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Acid Dissolution Method for the Analysis of Plutonium in Soil: Evaluation of an Interlaboratory Collaborative Test and Comparison with Results of a Fusion Method Test

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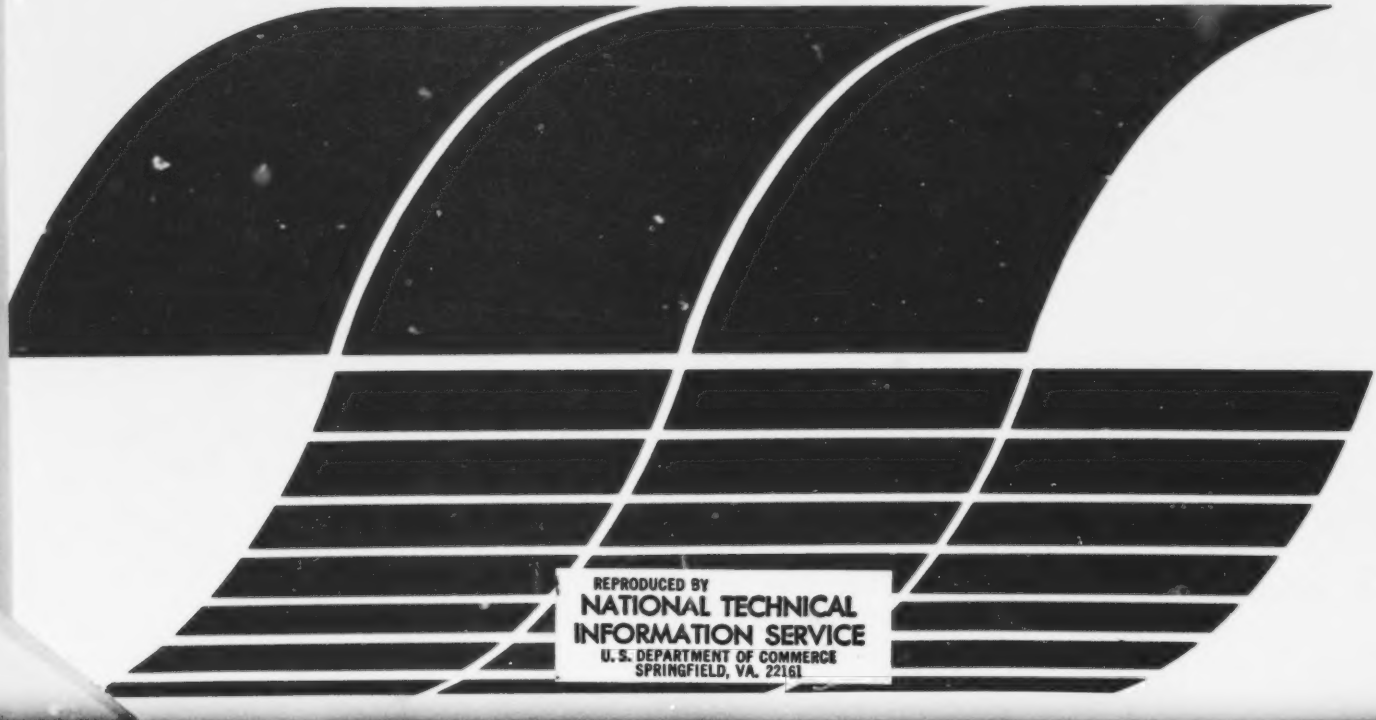

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March 1979

ACID DISSOLUTION METHOD FOR THE ANALYSIS OF PLUTONIUM IN SOIL

Evaluation of an Interlaboratory Collaborative Test and Comparison with Results of a Fusion Method Test

by

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FOREWORD

Protection of the environment requires effective regulatory actions which are based on sound technical and scientific information. This information must include the quantitative description and linking of pollutant sources, transport mechanisms, interactions, and resulting effects on man and his environment. Because of the complexities involved, assessment of specific pollutants in the environment requires a total systems approach which transcends the media of air, water, and land. The Environmental Monitoring and Support Laboratory-Las Vegas contributes to the formation and enhancement of a sound monitoring data base for exposure assessment through programs designed to:

- develop and optimize systems and strategies for monitoring pollutants and their impact on the environment
- demonstrate new monitoring systems and technologies by applying them to fulfill special monitoring needs of the Agency's operating programs.

This report presents the results of an Interlaboratory Collaborative test of an acid-dissolution method for measuring the plutonium concentrations in soil type samples when the plutonium on the soil is in a very insoluble refractory form. Those results are compared with the analytical results of a classical fusion method. The purpose of the comparison is to show equivalency of two methods, one being a shorter and less expensive method. Since the chemical form of plutonium in the environment is not always predictable, this report should be of interest to all analysts and others responsible for monitoring soil for plutonium contamination. For further information contact the Quality Assurance Branch of the Monitoring Systems Research and Development Division of the EMSL-Las Vegas.

George B. Morgan
Director
Environmental Monitoring and Support Laboratory
Las Vegas

ABSTRACT

The data from an interlaboratory collaborative test are presented. A statistical analysis of the data is also presented. From that analysis, statements are made of the combined within-laboratory precision, the systematic error between laboratories, the total error between laboratories based on a single analysis, and the method bias.

Soil samples used for the test contained plutonium in a highly refractory form, a very insoluble form, and therefore, difficult to measure the true concentration. Plutonium concentrations in those samples ranged from 0.1 to 10 dpm/g of soil.

A comparison is made between the acid dissolution method and a fluoride-pyrosulfate fusion method which was tested in a similar study using the same test samples.

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INTRODUCTION

In response to the need for the U.S. Environmental Protection Agency (EPA) to promulgate a guideline for the protection of people against harmful health effects resulting from soil contaminated with plutonium, a method of analysis has been tested and published (Hahn et al, 1977). To ensure the dissolution of very insoluble refractory forms, that method (a sequential fluoride pyrosulfate fusion method) is necessarily a tedious and rigorous exercise in analytical chemistry which, for large numbers of samples, would involve considerable time and expense. It was economically expedient then that another method be selected and tested which required less time and cost of materials. The method selected (an acid dissolution method) had been developed by the U.S. Atomic Energy Commission (now The Department of Energy) as its regulatory guide for the measurement of plutonium in soil (AEC Regulatory Guide 4.5, May 1974). This method is described in the Appendix to this report.

The results of an interlaboratory collaborative test of the acid dissolution method and a comparison with results of the fusion method are reported here. A statement is made of the equivalency of the two methods.

SUMMARY

The method in detail form, as tested, and as given in this report (Appendix), was documented by the Methods Development and Analytical Support Branch of the Monitoring Systems Research and Development Division of the Environmental Monitoring and Support Laboratory (EMSL-Las Vegas). The interlaboratory collaborative test was conducted by the Quality Assurance Branch of the same Division.

The AEC 4.5 method is an acid dissolution method, considerably simpler in detail than the sequential fluoride-pyrosulfate fusion method, and is widely used. A concern in the selection of the acid dissolution method, and the reason for a comparative study of the two methods, was whether or not the acid dissolution method would dissolve the highly refractory forms of plutonium and thereby account for such forms in the analysis. It is required that an EPA recommended method account for the insoluble forms of plutonium since the chemical form of environmental plutonium cannot always be predicted. It is believed by a number of the users of the acid dissolution method that it will account for the highly

refractory forms of plutonium.

The reference soil materials that were prepared (by AEC's Health Services Laboratory at Idaho Falls, Idaho) for the interlaboratory collaborative test of the sequential fluoride-pyrosulfate fusion method were also used to test the acid dissolution method. See Hahn et al, 1977, Appendix page A-24 for the procedure for standard soils preparation. The identification codes of the reference soil samples for the test of the acid dissolution method were changed from what they were for the test of the fusion method.

Of 37 laboratories invited to participate in the collaborative test of the method, 15 indicated they would participate. Reference samples and standards were sent to the 15 laboratories. Analytical data were returned by 6 laboratories.

Summary data are also given for the test of the fusion method for a comparison of the results of the two methods.

CONCLUSIONS AND RECOMMENDATIONS

The question of the ability of the acid dissolution method to account for the highly refractory forms of plutonium has been answered in this study. Had the method failed to dissolve those refractory forms known to exist in the samples, the method would have shown a definite low bias. A comparison of the grand average values with the respective known values in Table 6 indicates that there is a positive but not serious bias in the results of the method. Also, in Table 15 the calculated values of t are all lower than the critical values of t, indicating no serious bias in the method for the range of plutonium activity of 0.1 - 10 disintegrations per minute per gram (dpm/g) of soil.

Analytical results of labs 4 and 5 were not used in the statistical analysis of the data in Tables 6, 13, and 15. Lab 5 data were rejected because 3 of the 4 mean values of the replicate data reported by Lab 5 failed the "extreme mean" test (Steiner, 1975). Lab 4 data were rejected because the data failed the "Ranked Results" test (Youden, 1975). It is obvious from observing the data in Table 6 that Labs 4 and 5 had a definite systematic error in their analytical effort in this study.

No elaborate comparison can be made here between the acid dissolution method and the fluoride-pyrosulfate fusion method because of the limited number of collaborators in the two studies. However, there is sufficient evidence to conclude that both methods are adequate methods for monitoring soil for plutonium. The data for the coefficients of variation (%) in Tables 13 and 14 indicate that the fusion method gave better precision than the acid dissolution method. A comparison of the known values to the grand average values in Tables 6 and 12 shows that the fusion method gave a little better accuracy than the acid dissolution method.

It should be noted that two of the laboratories that participated in the fusion method also participated in the acid dissolution method. Lab 1 of the acid dissolution method is lab 4 of the fusion method and lab 6 of the acid dissolution method is lab 5 of the fusion method. Table 17 gives a comparison of the results of those labs with the two methods. Lab 1 got notably better results with the acid dissolution method than it did (lab 4) with the fusion method. Lab 5 got slightly better results with the fusion method than it did (lab 6) with the acid dissolution method.

The acid dissolution method is a somewhat shorter method than the fusion method. One analyst made the observation that the acid dissolution method required only about one half of the time that was required for fusion method. For the sake of economics then, the acid dissolution method would be the one of choice, although other factors favor the fusion method.

Since neither method shows a significantly low bias, as might be anticipated by the knowledge of the refractory form of the plutonium activity in the samples, both methods are adequate for monitoring environmental soil for plutonium. Insufficient data in this study tend to magnify those indicated differences as shown by the data reported. A larger set of data from more participating laboratories would likely diminish those differences somewhat. The two methods, in the opinion of the authors, are essentially equivalent methods.

COLLABORATIVE TEST - CALCULATIONS AND DATA

In the interlaboratory collaborative test of the acid dissolution method, reference samples H, F, E and G are the same sample materials as samples A, B, C and D respectively in the fluoride-pyrosulfate fusion test. The plutonium-239 activity levels are 0.1 dpm/g (A/H), 1.0 dpm/g (B/F; C/E), and 10 dpm/g (D/G) in the reference samples. The plutonium-238 activity levels are only 1/65 of the plutonium-239 amounts and therefore only samples D/G are high enough to be measured (0.1 dpm/g level). In the tables, the activities given for samples H, F, E/A, B, C are plutonium-239 activities and the plutonium-238 and plutonium-239 activities are indicated separately for samples D/G by the designations D-8, D-9/G-8, G-9.

Standard solutions of plutonium-239, -238 and plutonium-236 were sent to each participating laboratory along with 35g of each reference soil material so that all labs could be calibrated to the same standard. The detailed acid dissolution method (Appendix) contains a section on calibration and standardization (as did the fusion method). Therefore no subsequent effort was made to ensure that all labs were in fact calibrated to the same standard.

Individual analytical results for replicate samples for the six labs are tabulated by sample designation in Tables 1-5. Also included in the tables for each lab are the averages of the replicate results, $\overline{X}_i$; the experimental

(within lab) standard deviation, S_i; and the ratio of the average value to the known value. $\overline{X}_i$ is simply the arithmetic mean of the replicate results of each lab. S_i is a measure of the precision for each lab for a given sample and is calculated from Equation 1.

$$S_i = [\Sigma(X_i - \overline{X}_i)^2/(n_i - 1)]^{\frac{1}{2}} \quad (1)$$

where X_i = the individual results reported by Lab i

$\overline{X}_i$ = the mean of the individual results for Lab i

n_i = the number of replicates reported by Lab i

Table 6 gives a summary of the data from Tables 1-5. It lists the mean values according to laboratory and sample. It gives a ranking of the mean values according to laboratory and sample and a sum score for each laboratory (Youden 1975). For six labs and five samples the lower and upper limits for the ranking score are 7 and 28 respectively. Such a ranking is used to identify laboratories which show a pronounced systematic error or bias. Table 6 presents the grand average of the mean values from four laboratories for each sample. Equation 2 (Steiner, 1975) was used to determine any extreme means in the data.

$$r_{10} = \frac{X_n - X_{(n-1)}}{X_n - X_1} \quad (2)$$

where X_n = the highest (suspect) value

$X_{(n-1)}$ = the next highest value

X_1 = the lowest value

For low values the numerator in Equation 2 would be the lowest (suspect) value subtracted from the next lowest value.

Table 6 also lists three specific standard deviations for each sample which are needed to evaluate the method as to the limits of error that can be expected when a typical group of analysts use the method. Those standard deviations are S_r, the combined within laboratory standard deviation; S_d, the standard deviation of the 4-lab mean value data for each sample; and S_b, the standard deviation of the systematic errors. S_r is calculated from Equation 3.

$$(\Sigma n_i - m) \quad Sr^2 = \sum^{m} \sum^{n_i} (X_i - \overline{X}_i)^2 \quad (3)$$

where n_i = the number of replicate analysis by Lab i

m = the number of labs

X_i = the individual results for Lab i

$\overline{X}_i$ = the mean value for the individual results of Lab i

S_d is calculated from Equation 4.

$$S_d = [\Sigma(\bar{\chi}_i - \bar{\chi})^2 / (m-1)]^{\frac{1}{2}} \quad (4)$$

where $\bar{\chi}$ = the grand average of the lab mean values

$\bar{\chi}_i$ = the mean value for the individual results of Lab i

m = the number of labs

S_b is calculated from Equation 5. (Youden 1975).

$$S_b = (S_d^2 - S_r^2/K)^{\frac{1}{2}} \quad (5)$$

where K = the number of replicate analyses on a given sample by the participating labs.

S_b values in Table 6 were calculated using K = 3. However, in labs where routine soil analyses are performed, a single analysis is apt to be the usual extent of plutonium determination. Therefore the precision for single analysis needs to be determined. For that determination S_d needs to be recalculated for single analysis in place of triplicate analyses. This was done using Equation 5 using K = 1 and rearranging the equation to

$$S_d = S_b^2 + S_r^2$$

$$S_d = (S_b^2 + S_r^2)^{\frac{1}{2}}$$

and recalculating S_d values for the samples in Table 6. The recalculated S_d values according to sample are

H	0.0246
F	0.304
E	0.407
G-9	3.66
C-8	0.0497

Then the coefficients of variation were determined using the general equation

$$CV = 100\ S/\ \bar{\chi} \quad (6)$$

The coefficients of variation for within-laboratory error were calculated using values for S_r in the equation; for systematic error between laboratories using values for S_b in the equation; and for the total error between laboratories based on a single analysis by using the recalculated values for S_d in the equation. Table 13 presents the coefficients of variation according to sample for the acid dissolution method. It can be compared with Table 14 which gives the same information for the fusion method. It should be noted that since only a few collaborators reported data in this study, there was a limited number of observations. Consequently, the coefficients of variation are very limited estimates of the precision.

Comparing the grand average values to the known values for each sample in Table 13 shows that there is a positive bias but not a serious bias to the data of the acid dissolution method. However, the data were subjected to the t-test (test for systematic error in a method) for all of the samples (representing three levels of plutonium activity) by using Equation 7 (Youden 1975).

$$t = (\bar{\chi} - R)\, m^{\frac{1}{2}}/S_d;\ m\text{-}1 \text{ degrees of freedom} \qquad (7)$$

where $\bar{\chi}$ = the grand average value for each sample

R = the known value

m = the number of collaborators

S_d = the standard deviation of the data (taken from Table 6)

For comparison, results of the t-test are presented in Table 15 for the acid dissolution method and in Table 16 for the fusion method.

All of the data for the tables for the fusion method was treated by the same calculations as for the acid dissolution method. The mean value of sample B for Lab 6 was rejected and not used in the statistical analysis for sample B because it failed the extreme mean test. That was the only mean value of Lab 6 that failed the test, therefore the other mean values for Lab 6 are included in the statistical analysis for the respective samples.

REFERENCES

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Table 1
Acid Dissolution Method
Test Sample H, PU-239
(Known Value: 0.113 ± 0.001 dpm/g)

Lab	Lab Values (dpm/g)	$\overline{X}i$ (dpm/g)	Si (dpm/g)	Ratio $\overline{X}$/Known
1	0.103			
	0.122	0.114	0.010	1.01
	0.117			
2	0.146			
	0.150	0.148	0.002	1.31
	0.148			
3	0.146			
	0.120	0.134	0.013	1.19
	0.135			
4	0.114			
	0.130	0.122	0.011	1.08
	0.008*			
5	8.70			
	1.9	5.90	3.55	52.2
	7.09			
6	0.173			
	0.182	0.173	0.010	1.53
	0.163			

*Rejected by T-test (ASTM D-2777) for 3 observations and 5% significance.

Table 2
Acid Dissolution Method
Test Sample F, PU-239
(Known Value: 0.901 ± 0.003 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{x}_i$ (dpm/g)	S_i (dpm/g)	$\bar{x}$/Known Ratio
1	0.929 0.944 0.810	0.894	0.073	0.99
2	1.30 1.11 1.28	1.23	0.104	1.37
3	1.04 0.965 0.954	0.985	0.044	1.09
4	0.503 0.303 0.460	0.422	0.105	0.47
5	4.85 4.07 4.51	4.48	0.391	4.97
6	1.05 0.999 0.894	0.980	0.078	1.09

Table 3
Acid Dissolution Method
Test Sample E, PU-239
(Known Value: 1.03 ± 0.01 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{X}_i$ (dpm/g)	S_i (dpm/g)	$\bar{X}$/Known Ratio
1	0.977 1.02 1.07	1.02	0.047	0.99
2	1.72 1.37 1.51	1.53	0.18	1.49
3	1.19 1.23 1.19	1.20	0.023	1.16
4	0.656 0.202 0.512	0.457	0.23	0.444
5	5.07 5.46 5.14	5.22	0.21	5.07
6	1.19 1.17 1.10	1.15	0.048	1.12

Table 4
Acid Dissolution Method
Test Sample G, PU-239 (G-9)
(Known Value: 8.99 ± 0.03 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{\chi}_i$ (dpm/g)	S_i (dpm/g)	Ratio $\bar{\chi}$/Known
1	8.72 8.84 8.80	8.78	0.061	0.98
2	13.0 13.0 12.6	12.9	0.23	1.43
3	10.5 9.73 9.60	9.95	0.49	1.11
4	2.61 3.01 3.23	2.95	0.31	0.33
5	4.74 4.52 4.58	4.61	0.11	0.51
6	10.0 10.1 9.15	9.77	0.54	1.09

Table 5
Acid Dissolution Method
Test Sample G, PU-238 (G-8)
(Known Value: 0.138I 0.001 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{X}_i$ (dpm/g)	S_i (dpm/g)	$\bar{X}$/Known Ratio
1	0.159			
	0.161	0.159	0.002	1.15
	0.157			
2	0.179			
	0.206	0.188	0.016	1.36
	0.179			
3	0.155			
	0.152	0.151	0.005	1.09
	0.145			
4	0.155			
	0.036	0.076	0.069	0.55
	0.036			
5	ND			
	ND	--	--	--
	ND			
6	0.126			
	0.148	0.128	0.019	0.93
	0.110			

Table 6
Summary of Results - Acid Dissolution Method

	Average Values ($\bar{\chi}_i$, dpm/g)					Ranked Results					
Lab	H	F	E	G-9	G-8	H	F	E	G-9	G-8	SCORE
1	0.114	0.894	1.02	8.78	0.159	1	2	2	3	4	12
2	0.148	1.23	1.53	12.9	0.188	4	5	5	6	5	25
3	0.134	0.985	1.20	9.95	0.151	3	4	4	5	3	19
4a	0.122	0.422	0.457	2.95	0.076	2	1	1	1	1	6
5a	5.90	4.48	5.22	4.61	---	6	6	6	2	(3)	23
6	0.173	0.980	1.15	9.77	0.128	5	3	3	4	2	17
Known	0.113	0.901	1.03	8.99	0.138	The limits for acceptance by the score of the ranked results are 7-28. Lab 4 results were therefore rejected in the statistical analysis.					
$\bar{\chi}$	0.142	1.02	1.22	10.35	0.156						
S_d	0.0253	0.201	0.313	2.37	0.0327						
S_r	0.00951	0.0787	0.0949	0.377	0.0126						
S_b	0.0247	0.196	0.308	2.36	0.0319						

[a] Labs 4 and 5 data were not used in the statistical analysis.

Table 7
Fusion Method
Test Sample A; PU-239
(Known Value: 0.113 ± 0.001 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{X}_i$ (dpm/g)	S_i (dpm/g)	$\bar{X}$/Known Ratio
1	0.178 0.089 0.067	0.111	0.059	0.98
2	0.12 0.09 0.10	0.103	0.015	0.91
3	0.223 0.157 0.160	0.180	0.037	1.59
4	0.136 0.140 --	0.138	0.003	1.22
5	0.13 0.13 0.11	0.123	0.012	1.09
6	0.12 0.09 0.10	0.103	0.015	0.91

Table 8
Fusion Method
Test Sample B, PU-239
(Known Value: 0.901 ± 0.003 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{\chi}_i$ (dpm/g)	S_i (dpm/g)	$\bar{\chi}$/Known Ratio
1	0.844			
	1.04	0.932	0.101	1.03
	0.910			
2	0.75			
	0.88	0.813	0.065	0.90
	0.81			
3	0.887			
	0.857	0.881	0.022	0.98
	0.899			
4	0.94			
	0.98	0.947	0.031	1.05
	0.92			
5	0.82			
	0.83	0.840	0.026	0.93
	0.87			
6	0.40			
	0.58	0.490	0.127	0.54
	--			

Table 9
Fusion Method
Test Sample C, PU-239
(Known Value: 1.03 ± 0.01 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{X}_i$ (dpm/g)	S_i (dpm/g)	Ratio $\bar{X}$/Known
1	1.11 1.09 1.13	1.11	0.022	1.08
2	0.89 0.91 0.97	0.92	0.042	0.89
3	1.00 1.04 1.02	1.02	0.018	0.99
4	1.10 1.05 1.00	1.05	0.050	1.02
5	0.90 0.94 --	0.92	0.028	0.89
6	0.78 0.71 0.66	0.72	0.060	0.70

Table 10
Fusion Method
Test Sample D, PU-239 (D-9)
(Known Value: 8.99 ± 0.03 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{X}_i$ (dpm/g)	S_i (dpm/g)	$\bar{X}$/Known Ratio
1	11.3 9.32 9.32	9.98	1.14	1.11
2	8.4 8.4 7.9	8.23	0.29	0.92
3	8.21 8.22 8.12	8.18	0.058	0.91
4	9.71 9.17 9.29	9.39	0.28	1.04
5	7.79 8.26 --	8.02	0.33	0.89
6	7.03 6.65 6.30	6.66	0.36	0.74

Table 11
Fusion Method
Test Sample D, PU-238 (D-8)
(Known Value: 0.138 ± 0.001 dpm/g)

Lab	Lab Values (dpm/g)	$\bar{X}_i$ (dpm/g)	S_i (dpm/g)	Ratio $\bar{X}$/Known
1	0.244			
	0.133	0.185	0.056	1.34
	0.178			
2	0.12			
	0.12	0.113	0.012	0.82
	0.10			
3	ND			
	0.493			
	ND			
4	0.166			
	0.187	0.173	0.012	1.25
	0.167			
5	0.15			
	0.13	0.140	0.014	1.01
	--			
6	0.16			
	0.13	0.130	0.030	0.94
	0.10			

Table 12
Summary of Results - Fluoride - Pyrosulfate Fusion Method

Lab	Average Values ($\bar{\chi}_i$, dpm/g) A	B	C	D-9	D-8	Ranked Results A	B	C	D-9	D-8	SCORE
1	0.111	0.932	1.11	9.98	0.185	3	5	6	6	5	25
2	0.103	0.813	0.92	8.23	0.113	1.5	2	2.5	4	1	11
3	0.180	0.881	1.02	8.18	---	6	4	4	3	(3)	20
4	0.138	0.947	1.05	9.39	0.173	5	6	5	5	4	25
5	0.123	0.840	0.92	8.02	0.140	4	3	2.5	2	3	14.5
6	0.103	0.490a	0.72	6.66	0.130	1.5	1	1	1	2	6.5
Known	0.113	0.901	1.03	8.99	0.138	The limits for acceptance by the score of the ranked results are 7-28. Lab 6 score is close enough to 7, therefore was not rejected.					
$\bar{\chi}$	0.126	0.883	0.957	8.41	0.148						
s_d	0.0295	0.0576	0.138	1.160	0.0300						
s_r	0.0315	0.0571	0.0407	0.550	0.0418						
s_b	0.0232	0.0472	0.136	1.120	0.0178						

[a]This mean value was not used in the statistical analyses because it failed the extreme mean test.

Table 13
Summary of Precision Data
Acid Dissolution Method

Sample	Known (dpm/g)	$\overline{X}$ (dpm/g)	Coefficients of Variation (%) within lab	between labs	Total (single analysis)
H	0.113	0.142	6.7	17.4	18.7
G-8	0.138	0.156	8.1	20.4	22.0
F	0.901	1.02	7.7	19.2	20.7
E	1.03	1.22	7.8	25.2	26.4
G-9	8.99	10.35	3.6	22.8	23.1

Table 14
Summary of Precision Data
F1 - Pyrosulfate Fusion Method

Sample	Known (dpm/g)	$\overline{X}$ (dpm/g)	Coefficients of Variation (%) within lab	between labs	Total (single analysis)
A	0.113	0.126	25.0	18.4	31.0
D-8	0.138	0.148	28.2	12.0	30.7
B	0.901	0.883	6.5	5.3	8.4
C	1.03	0.957	4.3	14.2	14.8
D-9	8.99	8.41	6.5	13.3	14.8

Table 15
t-Test to Detect Method Bias
Acid Dissolution Method

Sample	m	t-calc.	t-crit.
H	4	2.29	3.18
G-8	4	1.10	3.18
F	4	1.18	3.18
E	4	1.21	3.18
G-9	4	1.15	3.18

Table 16
t-Test to Detect Method Bias
Fluoride - Pyrosulfate Fusion Method

Sample	m	t-calc.	t-crit.
A	6	1.08	2.57
D-8	5	0.75	2.78
B	5	0.70	2.78
C	6	1.30	2.57
D-9	6	1.23	2.57

Table 17
Comparison of Results for Two Laboratories
that Participated in Both Methods

% Deviation from the Known Value

Sample (dpm/g)	Lab 1 Acid Dissolution	Lab 4 Fusion	Lab 6 Acid Dissolution	Lab 5 Fusion
.113	0.88 (+)	22.1 (+)	53.1 (+)	8.8 (+)
.901	0.78 (-)	5.1 (+)	8.8 (+)	6.8 (-)
1.03	0.97 (-)	1.9 (+)	11.6 (+)	10.7 (-)
8.99	2.3 (-)	4.4 (+)	8.7 (+)	10.8 (-)
.138	15.2 (+)	25.4 (+)	7.2 (-)	1.4 (+)

APPENDIX

TENTATIVE METHOD FOR THE ANALYSIS OF PLUTONIUM-239 AND PLUTONIUM-238 IN SOIL (Acid Dissolution Technique)

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The method described in this Appendix was distributed to the participating laboratories for the interlaboratory collaborative test.

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PREFACE

The analytical method described in this document was developed by the U.S. Atomic Energy Commission as their Regulatory Guide Method for the measurement of plutonium in soil.

The method was selected for collaborative testing on the basis of both theoretical considerations and its widespread use to determine its suitability as an Environmental Protection Agency Reference Method. Data from the collaborative tests will be used to determine, on a statistical basis, the limits of error which can be expected when the method is used by a typical group of analysts.

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Figure 1 Disposable Electrodeposition Cell and Support

SOIL ANALYSIS PROCEDURE

1. SCOPE AND APPLICATION

1.1 This method covers the analysis of soils for plutonium at levels greater than 0.01 dpm/g in a variety of chemical and physical forms known to exist in soils encountered in the United States. The method is expected to adequately handle soils containing plutonium in a non-refractory form and there is documented evidence that the method should also be applicable to soils containing certain refractory forms of plutonium (U.S. Atomic Energy Commission Regulatory Guide 4.5, May 1974), (Sill 1975b).

1.2 The minimum detection level (MDL) of the method will depend on both the background counting rate of the alpha spectrometer and the amount of plutonium-238 and plutonium-239 contamination in the plutonium-236 tracer. Plutonium-236 having only a few hundredths percent of plutonium-238 and plutonium-239 contamination is now commercially available and is recommended for this procedure. For an analysis of 10 g of soil, employing 10 dpm of plutonium-236 tracer, a 1000-minute counting time on a spectrometer having a 17% counting efficiency and a 0.010-cpm background over each energy region of interest, and realizing an 80% plutonium recovery, the MDL is estimated to be 0.008 dpm/g.

1.3 The precision and accuracy of the method have not, as yet, been extensively documented. The method is proposed for interlaboratory collaborative test to determine the limits of precision and error which can be expected when it is used by a typical group of analysts.

1.4 This method is recommended for use by experienced technicians under the supervision of a radiochemist or other qualified person who fully understands the concepts involved in the analysis and instrument calibrations. Furthermore, the method should be utilized only after satisfactory results are obtained by the analyst when replicate standard soil samples are analyzed.

2. SUMMARY

2.1 The principle of the analytical procedure follows (U.S. ...omic Energy Commission Regulatory Guide 4.5, May 1974): A known quantity of plutonium-236 tracer is added to the sample which is decomposed by sequential nitric acid-hydrofluoric acid and nitric acid-hydrofluoric acid-hydrochloric acid digestions. Boric acid is added to complex the fluoride ion and to aid in the extraction of plutonium from any remaining insoluble residue. Sequential iron hydroxide precipitations are performed with sodium hydroxide and ammonium hydroxide to respectively remove amphoteric elements and calcium and to eliminate soluble fluorides. The hydroxide precipitate is dissolved in nitric acid saturated with boric acid and plutonium is isolated and purified by two successive anion exchange separations. The

plutonium is electroplated on stainless steel disks and is determined by alpha spectrometry. The chemical yield, counting efficiency, counting time, etc., are the same for all plutonium isotopes and simplify calculations. In addition to the activity of plutonium-236 added and the weight of the sample, only the total number of counts of plutonium-236, plutonium-239, and/or plutonium-238 recovered is necessary to calculate the concentration of plutonium-239 and/or plutonium-238 in the sample.

3. INTERFERENCES

3.1 Reagents, glassware, and other sample processing hardware may cause contamination. All of these materials must be demonstrated free from contamination under the conditions of the analysis. Specific selection of reagents and sample processing hardware is detailed in the procedure.

3.2 Possible procedural interferences are noted when apt to be encountered.

4. APPARATUS

4.1 Instrumentation and Accessories (as described or functionally equivalent)

4.1.1 A windowless 2π gas flow proportional counter.

4.1.2 An alpha spectrometer capable of 40- to 50-keV resolution of actual samples electrodeposited on flat, mirror-finished stainless-steel planchets with a counting efficiency greater than 17% and a background less than 0.010 cpm over each designated energy region. Resolution is defined as the full width half maximum (FWHM) in keV, the distance between

those points on either side of the alpha peak where the count is equal to one-half the maximum count (Heath, 1964).

4.1.3 Disposable electrodeposition cells are constructed from 20-ml, linear-polyethylene, liquid scintillation vials. See Figure 1. A 1.59-cm (5/8-inch) hole is cut in the bottom for introduction of the anode. The foil-lined caps are replaced by 22-mm Polyseal caps having a GCMI 400 thread design. The tubular portion of the polyethylene liner is removed and the conical portion retained as a cover for the assembled cell. A 0.36-cm (9/64-inch) hole having a beveled inside edge is bored through the center of the cap. A 1.91-cm (3/4-inch) diameter washer with a 0.32-cm (1/8-inch) hole is cut from 0.08-cm (1/32-inch) neoprene and placed in the cap. The shank of a hollow brass rivet (Dot Speedy Rivets, #BS4830, Carr Fastener Co., Cambridge, Massachusetts) is passed through the washer and cap to serve as an electrical contact for the planchet cathode, (Talvitie, 1974). The cell support and cathode socket consist of a non-insulating banana jack attached to a Lucite base.

4.1.3.1 The cathodes are 1.91-cm (3/4-inch) diameter, 0.38-mm (15-mil) thick, type 304 stainless steel planchets pre-polished to a mirror finish. The exposed cathode area is 2.3 cm^2. Prior to use the planchets are degreased with detergent and/or acetone, immersed in hot concentrated nitric acid for 10 minutes, rinsed, and stored under distilled water until needed.

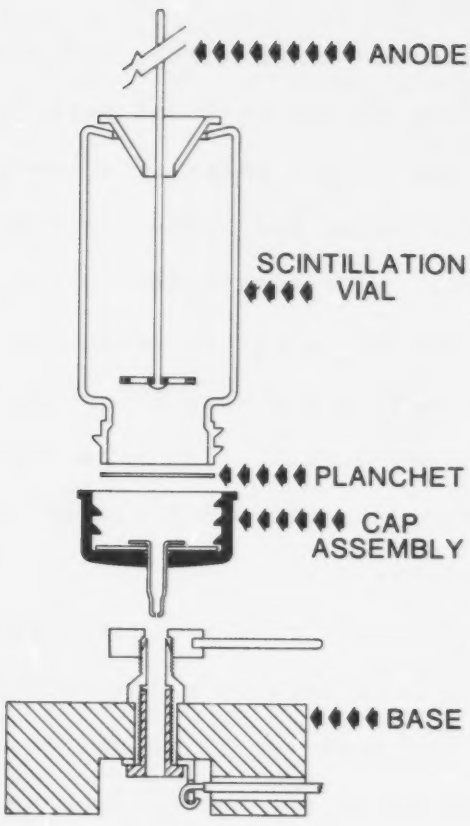

Figure 1. Disposable electrodeposition cell and support

4.1.3.2 The anode is a 1.27-cm (1/2-inch) diameter, 0.08-cm (1/32-inch) platinum or platinum-iridium disk having six 0.32-cm (1/8-inch) perforations and attached at the center to a 10-cm (4-inch) length of 0.16-cm (1/16-inch) platinum or platinum-iridium rod.

4.1.3.3 To assemble the cell, the planchet is centered on the threaded end of the cell and held in place by vacuum applied through one of the holes of a two-hole rubber stopper butted against the other end. The cap assembly is screwed on and leakage checked by adding water to the cell and observing the rise of air bubbles when the vacuum is reapplied. Flexing the cell by alternately applying and releasing the vacuum improves the seal of leaky cells. The combined resilience of planchet and washer maintains the liquid seal and electrical contact during electrolysis.

4.1.3.4 Electrolysis is conducted without stirring using an electroplating unit such as a 10-volt, 5-ampere Sargent-Slomin Electrolytic Analyzer. The platinum anode is lowered into the solution until the bottom edge of the anode is about 2 mm above the shoulder of the cell. (If set too deeply, gas bubbles will be trapped and cause fluctuations of the current.)

4.2 Laboratory Equipment (as described or equivalent)

4.2.1 Pulverizer -- Arthur H. Thomas 3367-D05 pulverizer, pulverizes one pound quartz ore 0.64 cm in diameter to 0.15 mm (100 mesh) in one minute, requires 1-hp motor.

4.2.2 Balance -- Mettler top-loading balance, capacity

1200 g, precision ± 0.05 g.

4.2.3 Drying oven -- maximum temperature 110°C, including trays to fit.

4.2.4 Infrared drying lamp.

4.2.5 Centrifuge -- for 220-ml centrifuge bottles.

4.2.6 Hot plate -- capable of providing a temperature range of 10° above ambient to 370°C.

4.2.7 Burner -- Meker type.

4.2.8 Hot water bath -- to accommodate 220-ml centrifuge bottles.

4.2.9 Anion exchange resin columns -- Dowex 1 x 4 (100-200 mesh nitrate form). Remove the fines from an appropriate amount of resin by repeated suspension in distilled water and decantation. Decant the water and add a volume of concentrated (16 M) nitric acid approximately equal to 50% of the volume of the resin slurry. Using 8 M nitric acid from a wash bottle, transfer sufficient resin to a 1.3 cm ID ion exchange column to give a 10-cm bed of settled resin. Convert the resin to the nitrate form by passing 100 ml of 8 M nitric acid through the column at maximum flow rate.

4.3 Labware (as described or functionally equivalent)

4.3.1 Pipets.

4.3.1.1 Automatic pipets with disposable tips -- optional sizes.

4.3.1.2 Disposable pipets -- 2-ml glass eye-dropper type, with 2-ml bulb.

4.3.1.3 Volumetric -- 1 ml, treated with silicone water repellent to eliminate drainage and calibrated "to contain" by blowing residual liquid from the tip.

4.3.2 Dropping bottles.

4.3.3 Beakers -- glass, 150 ml, 250 ml and other assorted sizes.

4.3.4 Beakers -- PTFE "Teflon," 250 ml.

4.3.5 Graduated cylinders -- assorted sizes.

4.3.6 Ion exchange columns -- 1.3 cm ID x 15 cm with reservoir to hold 100 ml of solution.

4.3.7 Centrifuge bottles -- 220-ml capacity.

4.3.8 Millipore filter holder -- Pyrex, to accommodate 47-mm filter.

4.3.9 Membrane filters -- 47-mm diameter, 0.45 µm pore size DM-450.

4.3.10 Polyethylene wash bottles -- optional sizes.

4.3.11 Teflon IEP bottles -- optional sizes.

4.3.12 Safety glasses.

4.3.13 Timer -- minute intervals.

4.3.14 Scissors.

4.3.15 Spatulas -- optional sizes.

4.3.16 Rubber policemen.

4.3.17 Stirring rods -- Teflon and glass.

4.3.18 Stainless steel planchets -- 5.0 cm and 1.91 cm disks pre-polished to a mirror finish on one side.

4.3.19 pH paper -- pH range 1-12.

5. STANDARDS, ACIDS, REAGENTS

5.1 Standards

5.1.1 National Bureau of Standards (NBS) americium-241 point source -- approximately 3×10^5 dpm, deposited on platinum and certified to ± 1% of its stated activity.

5.1.2 Plutonium-236 solution -- 2.5×10^4 dpm of plutonium-236 in 2 M nitric acid in minimal solution (available from Oak Ridge National Laboratory).

5.1.3 Americium-241 solution -- 1×10^5 dpm of americium-241 in 2 M nitric acid in minimal solution.

5.2 Acids

All solutions are made with distilled water. All acids are reagent grade and meet American Chemical Society (ACS) specifications.

5.2.1 Boric acid -- crystalline.

5.2.2 Hydrochloric acid -- concentrated (12 M), 4 M and 2 M.

5.2.3 Hydrofluoric acid -- concentrated (48% solution).

5.2.4 Nitric acid -- concentrated (16 M), 8 M, 8 M saturated with boric acid and 2 M.

5.3 Reagents

All solutions are made with distilled water. All reagents listed are reagent grade and meet ACS specifications unless otherwise defined.

5.3.1 Ammonium hydroxide -- concentrated (15 M).

5.3.2 Ammonium iodide-hydrochloric acid solution -- 1 part 1 M ammonium iodide to 20 parts 12 M hydrochloric acid.

5.3.3 Anion exchange resin -- Dowex 1 x 4 (100-200 mesh, nitrate or chloride form).

5.3.4 Iron carrier -- 10 mg Fe(III)/ml in 2 M hydrochloric acid.

5.3.5 Octyl alcohol.

5.3.6 Silicone water-repellent solution.

5.3.7 Sodium bisulfite -- anhydrous.

5.3.8 Sodium nitrite -- crystalline.

5.3.9 Sodium hydroxide -- 50% solution.

5.3.10 Thymol blue indicator, sodium salt -- 0.02% solution.

6. CALIBRATION AND STANDARDIZATION

6.1 Calibration of the 2π Alpha Counter and the Alpha Spectrometer (Sill, 1974).

6.1.1 The windowless, 2π alpha counter is standardized by counting the NBS americium-241 source to approximately 5×10^5 total counts.

6.1.2 The efficiency of the 2π alpha counter is calculated by dividing the observed counts per minute (cpm) by the certified disintegrations per minute (dpm) of the NBS americium-241 source.

6.1.3 Correct the counting efficiency for the difference in backscatter between platinum and stainless steel by dividing the calculated efficiency (from 6.1.2) by 1.023, (Hutchinson,

1968), (Sill, 1975a).

6.1.4 Because a point-source standard electrodeposited on platinum -- the NBS americium-241 source -- cannot be used to calibrate an alpha spectrometer with an external detector for use with diffuse sources electrodeposited on stainless steel, a secondary standard must be employed. Prepare a secondary standard containing about 1×10^4 dpm of americium-241 electrodeposited on stainless steel under the exact conditions subsequently described for electrodeposition of samples.

6.1.5 Standardize the secondary standard by counting in the 2π counter until at least 2×10^5 counts have been collected.

6.1.6 Use the secondary standard to calibrate the alpha spectrometer and to periodically check the initial calibration of both the spectrometer and the 2π counter.

6.2 Purification of the Plutonium-236 Tracer, (Sill, 1970). (U.S. Atomic Energy Commission Regulatory Guide 4.5, May, 1974)

In order to accurately calibrate the plutonium-236 tracer by 2π counting and alpha spectrometry, it will be necessary to ensure the absence of plutonium-236 daughters (uranium-232, thorium-228, radium-224, etc.) in the tracer. The following purification must be performed just prior to the initial calibration and annually thereafter if additional calibrations are desired.

6.2.1 Add approximately 2.5×10^4 dpm of plutonium-236 to a 250-ml beaker containing 25 ml of 16 M nitric acid.

6.2.2 Evaporate the solution on a hotplate to a volume of approximately 10 ml.

6.2.3 Remove from the hotplate and add 25 ml of 8 M nitric acid and 10 ml of distilled water to adjust the nitric acid concentration to 8 M.

6.2.4 Add ∿200 mg of sodium nitrite crystals and stir with a glass stirring rod. Bring the solution to a quick gentle boil on a hotplate, and cool. Avoid prolonged heating.

6.2.5 Pass through an anion-exchange resin column (nitrate form) prepared as described in 4.2.9 at maximum flow rate.

6.2.6 When the solution just drains to the top of the resin bed, add two column volumes of 8 M nitric acid to the column reservoir and wash the resin column at the maximum flow rate. Discard the effluents from the sample and washes. NOTE: The exact volumes of reagents used in the ion exchange separations are critical and will vary according to the column size and the quantity of resin used. Determine the volume of the 10 cm resin bed and use the appropriate number of column volumes of reagents in all steps.

6.2.7 Repeat step 6.2.6 twice until the resin column has been washed with a total of six column volumes of 8 M nitric acid.

6.2.8 Wash the resin column at maximum flow rate with six column volumes of 12 M hydrochloric acid using the same technique. Discard the hydrochloric acid washes.

6.2.9 Elute the plutonium with four column volumes of freshly-prepared ammonium iodide-hydrochloric acid solution (1 part 1 M NH_4I to 20 parts 12 M HCl) and collect in a 150-ml beaker.

6.2.10 Evaporate the solution to approximately 5 ml on a hotplate. Rinse down the sides of the beaker dropwise with 1-2 ml of 16 M nitric acid. Add six drops of 12 M hydrochloric acid and evaporate just to dryness on the hotplate.

6.2.11 Add 5 ml each of concentrated hydrochloric and nitric acids to the beaker and evaporate to about 2 ml.

6.2.12 Add 15 ml of concentrated nitric acid and boil down to about 5 ml to ensure complete dissolution of the plutonium and complete oxidation of chlorides as indicated by the absence of color or fumes of chlorine and/or nitrogen oxides.

6.2.13 Cool, add 25 ml of distilled water and filter the solution through a DM-450 membrane filter in a filtering chimney. Wash the flask and filter with enough distilled water to give a final volume of 50 ml.

6.2.14 Dilute aliquots of the ∿500 dpm/ml stock solution with 2 M nitric acid to give concentrations desired for use. Store all tracers in tightly capped Teflon FEP bottles.

6.3 Standardization of the Plutonium-236 Tracer (Sill, October, 1974)

6.3.1 Transfer a 1-ml aliquot of the purified plutonium-236 stock tracer (∿500 dpm/ml in 2 M nitric acid) onto a stainless steel planchet with a calibrated silicone-treated pipet and slowly evaporate to near dryness under an infrared lamp to minimize any loss. Keep the activity in the center of the planchet in an area limited to approximately 2 cm (3/4 inch) in diameter by alternately adding the tracer a few drops at a time and evaporating. The partially-filled

silicone-treated pipet can be placed on its side between additions with no loss of solution. To ensure quantitative transfer of the tracer, carefully blow out the last few drops with a rubber bulb.

6.3.2 When the last of the tracer has been transferred to the planchet and evaporated nearly to dryness, add 2 or 3 drops of concentrated nitric acid to help keep the activity spread as uniformly as possible and evaporate to complete dryness.

6.3.3 Heat the dry planchet over a blast burner just to the first dull red glow. Then quickly lower the temperature by placing the planchet on a cold steel surface to minimize oxidation of the plate.

6.3.4 Count in the 2π alpha counter immediately after cooling to avoid any possibility of absorption of water vapor from the air. Collect at least 5×10^4 counts for the standard to ensure adequate statistical precision.

6.3.5 Prepare and count a duplicate source by repeating steps 6.3.1 through 6.3.4.

6.3.6 The 2π counting rate of the plutonium-236 sources must be corrected by determining the fraction of the total alpha activity due to plutonium-236.

6.3.6.1 Transfer 2 ml of the purified $\sim$500 dpm/ml plutonium-236 tracer to a 150-ml beaker and add 2 ml each of concentrated nitric acid and hydrochloric acid.

6.3.6.2 Evaporate carefully on a hot plate just to

dryness. Rinse down the sides of the beaker with a few ml of 12 M hydrochloric acid and evaporate to approximately 1/2 ml.

6.3.6.3 Treat and electrodeposit as described in Sections 7.5.1 through 7.5.8.

6.3.6.4 Count the electroplated source on an alpha spectrometer for 250 minutes over an energy range of 3-8 MeV. Determine the fraction of the total number of counts in the alpha spectrum that is due to plutonium-236 in the source. This fraction is the correction factor to be applied to the counting rate of the plutonium-236 evaporated source in the 2π proportional counter. NOTE: Prolonged and repeated counting of high level plutonium-236 sources on the alpha spectrometer should be avoided to minimize daughter recoil contamination of the alpha detector. Alternatively, such contamination can be virtually eliminated by leaving a small amount of air in the counting chamber and applying a small negative potential to the source plate. (Sill, November 1970)

6.3.7 Calculate the activity concentration of the plutonium-236 tracer (dpm plutonium-236/ml) by multiplying the observed 2π counting rates of the evaporated sources by the correction factor and dividing by the 2π counter efficiency and the volume of tracer used to prepare the evaporated sources.

7. STEP BY STEP PROCEDURE FOR ANALYSIS (U.S. Atomic Energy Commission Regulatory Guide 4.5, May 1974)

7.1 Sample Decomposition

7.1.1 Weigh a representative 10.0 ± 0.1 grams of the

-100 mesh soil sample and transfer to a 250-ml PTFE beaker.

7.1.2 Add 16 M nitric acid a few drops at a time as fast as the frothing and vigor of the reaction will permit until the entire sample is covered.

7.1.3 Add an appropriate quantity of plutonium-236 tracer. NOTE: If the activity is expected to be less than 1 dpm/g, or is unknown, add 10 dpm of the tracer. For higher levels add as much plutonium-236 tracer as the estimated activity of plutonium-239 or plutonium-238 in the sample.

7.1.4 Add an additional 60 ml of 16 M nitric acid and 30 ml of 48% hydrofluoric acid and digest on a hotplate with frequent stirring (Teflon stirring rod) for about 1 hour. CAUTION: Hydrofluoric acid is an extremely hazardous liquid. Use gloves to avoid contact with skin and work in a fume hood to avoid breathing vapors. NOTE: For organic soils, first add the nitric acid only, in small portions, with stirring. If the solution threatens to overflow as a result of froth generation, add a few drops of octyl alcohol and stir. Digest on a hotplate until the evolution of heavy reddish-brown fumes is reduced to a barely visible level. Cool to room temperature before carefully adding the hydrofluoric acid and digesting for the one-hour period.

7.1.5 Remove from the hotplate and cool somewhat before adding 30 ml each of 16 M nitric acid and 48% hydrofluoric acid. Digest on the hotplate with intermittent stirring for an additional hour.

7.1.6 Remove from the hotplate and cool. Carefully add 20 ml of 12 M HCl and stir. Heat on a hotplate for 45 minutes with occasional stirring.

7.1.7 Add 5 g of powdered boric acid and digest for an additional 15 minutes with occasional stirring.

7.1.8 Add approximately 200 mg of sodium bisulfite crystals and continue heating until the solution has evaporated to a liquid volume of approximately 10 ml.

7.1.9 Add 50 ml of distilled water and digest on a hotplate with stirring for 10 minutes to dissolve the soluble salts.

7.2 Sodium Hydroxide Precipitation

7.2.1 Cool and transfer approximately equal parts of the total sample into two 220-ml centrifuge bottles with a minimum of distilled water from a wash bottle. NOTE: If equipment for large volume centrifugation is not available, the following two precipitations may be performed in a beaker, allowing the precipitate to settle, decanting the supernate, and then completing the separation by centrifugation on a smaller scale.

7.2.2 Add 1 ml of iron carrier solution (10 mg Fe^{3+}/ml) to each centrifuge bottle and stir.

7.2.3 Add 50% sodium hydroxide with stirring to each bottle to a pH of ~9. Add 5-10 ml excess of the sodium hydroxide and stir for 1 minute.

7.2.4 Centrifuge for approximately 5 minutes, decant and discard the supernate(s).

7.2.5 Dissolve each precipitate with about 30 ml (60 ml total) of 8 M nitric acid saturated with boric acid. Digest on a hot water bath for 10 minutes.

7.2.6 Cool and centrifuge for 5 minutes. Decant the supernates into the original 250-ml PTFE beaker and save.

7.2.7 Wash each residue with approximately 10-20 ml (20-40 ml total) of 8 M nitric acid saturated with boric acid. Centrifuge for 5 minutes and combine the supernates with those in step 7.2.6.

7.2.8 Heat the supernates on a hotplate and evaporate to near dryness.

7.3 Ammonium Hydroxide Precipitation

7.3.1 Add approximately 30 ml of water and heat to dissolve the salts. Cool, and transfer equal portions into centrifuge bottles.

7.3.2 Add 15 M ammonium hydroxide dropwise with stirring to a pH of ∿9.

7.3.3 Centrifuge and discard the supernate.

7.4 Ion Exchange Separations

7.4.1 Dissolve the precipitate(s) with a volume of 16 M nitric acid approximately equal to the volume of the precipitate(s) and transfer using 8 M nitric acid into a 250-ml beaker. Add 8 M nitric acid to a total volume of approximately 75 ml. NOTE: If the volume of the hydroxide precipitate is considerably greater than should be expected from the 10 mg of Fe added, the final volume should be brought up to approximately 100 ml

with 8 M nitric acid or, alternatively, the dissolved hydroxides should be evaporated to salts before addition of the 8 M nitric acid solution. The final molarity of the HNO_3 is not extremely critical, but should be in the range of 7-9.

7.4.2 Add approximately 200 mg of sodium nitrite ($NaNO_2$) crystals and stir with a stirring rod. Bring to a quick gentle boil on a hotplate, and cool. Avoid prolonged heating.

7.4.3 Pass the sample (at maximum flow rate) through an anion-exchange resin column (nitrate form) prepared as described in 4.2.9.

7.4.4 When the solution just drains to the top of the resin bed, add two column volumes of 8 M nitric acid to the column reservoir and wash the resin column at maximum flow rate. Discard the effluents from the sample and washes.

7.4.5 Repeat step 7.4.4 twice until the resin column has been washed with a total of six column volumes of 8 M nitric acid. NOTE: See 6.2.6 note.

7.4.6 Wash the resin column with six column volumes of 12 M hydrochloric acid using the same technique. Discard the hydrochloric acid washes.

7.4.7 Elute the plutonium with four column volumes of freshly-prepared ammonium iodide-hydrochloric acid solution (1 part 1 M NH_4I to 20 parts 12 M HCl) and collect in a 150-ml beaker.

7.4.8 Evaporate the solution to approximately 5 ml on a hotplate. Rinse down the sides of the beaker dropwise with

1-2 ml of 16 M nitric acid. Add six drops of 12 M hydrochloric acid and evaporate to near dryness.

7.4.9 Add 50 ml of 8 M nitric acid and repeat steps 7.4.2 - 7.4.8, using a fresh anion-exchange resin column (nitrate form).

7.4.10 Continue heating the final plutonium elution just to dryness on the hotplate. Rinse down the sides of the beaker with a few ml of 12 M hydrochloric acid and evaporate to approximately 1/2 ml.

7.5 Electrodeposition

7.5.1 Add 1 1/2 to 2 ml of 4 M hydrochloric acid into the beaker and using a disposable pipet (2-ml glass eyedropper type, with 2-ml bulb), rinse down the sides of the beaker with the sample solution. Transfer the solution into a plating cell.

7.5.2 Add another 1 1/2 to 2 ml of 4 M hydrochloric acid into the beaker, rinse as above and add to the plating cell.

7.5.3 Repeat using approximately 1 ml of distilled water.

7.5.4 Add 3 drops of thymol blue indicator solution and then add 15 M ammonium hydroxide dropwise until the color changes to yellow.

7.5.5 Add 2 M hydrochloric acid dropwise to a salmon-pink end point.

7.5.6 Electroplate at 1.5 amps for 20 minutes. CAUTION: The electrodeposition should be performed in a fume hood due to the chlorine gas evolved during the electrodeposition.

7.5.7 At the end of 20 minutes, quickly add 2-3 ml of

concentrated NH_4OH and leave the current on for another 20 seconds.

7.5.8 Turn the current off, rinse out the solution into a beaker with distilled water, and dismantle the cell. Rinse the disc with distilled water and dry it in a clean planchet on a hotplate at medium heat for 5 minutes.

7.5.9 Count the sample in an alpha spectrometer to resolve the isotopes of plutonium. For samples containing less than 1 dpm/g of plutonium a minimum of 1.5×10^3 counts should be collected for the plutonium-236 tracer. For higher levels, count for 1000 minutes or until 10^4 counts have been collected in each of the plutonium-236 and the plutonium-239 and/or plutonium-238 energy regions.

7.6 Quality Assurance Program

For any analytical procedure a rigorous quality assurance program must be followed to ensure accurate and precise results. Such a program must include the evaluation of all variables in the final calculation for their degrees of uncertainty and for any significant systematic errors. Precautions must be taken to eliminate any cross contamination between samples, especially if high and low level samples are run concurrently. Standard samples should be analyzed both to check out initial capabilities and to provide for a continuing quality control program.

7.6.1 The internal laboratory precision of the method is evaluated by considering the uncertainties in all the variables in the final calculation. These include the counting uncer-

tainties associated with counting the sample and the standards for calibration, uncertainties associated with pipettings and tracer dilutions and weighing the original sample, and any uncertainty in the timing of the 2π count during the calibration. All uncertainties should be evaluated and if significant, propagated to the final result. Variability between laboratories is expected to be greater than that for a single laboratory due to the variability in NBS standards used for calibration, slight differences in calibration procedures, etc. The interlaboratory precision of the method can be adequately estimated only on the basis of collaborative testing. Systematic errors in the method will be minimized by calibrating all pipets, volumetric flasks, and balances used for the tracer calibration and sample analysis, and by calibrating the 2π counter timing mechanism. The systematic error introduced by the ± 1% uncertainty in the NBS standard and the error in the backscatter correction factor cannot be compensated for.

7.6.2 Cross contamination of samples may be avoided with good housekeeping and by either segregating apparatus used for high- and low-level samples, or by carefully decontaminating glassware and Teflon ware between analyses. Contamination of stock reagents must be avoided. This can best be accomplished by employing intermediate containers to which small portions of the stock reagents can be transferred before adding to the sample. The excess reagent is then discarded and the intermediate container rinsed before reuse. Reagent blanks using the

same reagents, tracer, glassware, Teflon ware, electrodeposition equipment and detector must be run initially and periodically thereafter to determine the radiochemical background for the method and ascertain that contamination of these items has not occurred.

8. CALCULATION OF RESULTS (Overman 1960, Sill 1975a)

8.1 CALIBRATION OF THE 2π ALPHA COUNTER

8.1.1 The counting efficiency of the 2π counter is determined by counting an NBS certified americium-241 source electrodeposited on a platinum disk.

8.1.2 The 2π counting efficiency ($E_{2\pi}$) is calculated as:

$$E_{2\pi} = \frac{c_1}{(a_1)(t)(1.023)} \qquad (8.1.1)$$

in which c_1 = the net counts of the americium-241 source,

a_1 = the certified activity of the americium-241 source (dpm),

t = the duration of the count (min)

and 1.023 = the backscatter factor correcting the counting efficiency of a source on platinum to that on stainless steel.

8.2 STANDARDIZATION OF THE PLUTONIUM-236 TRACER

8.2.1 The purified plutonium-236 stock tracer is standardized by counting evaporated sources on the 2π counter and an electrodeposited source on the alpha spectrometer. The 2π count which represents total activity is corrected by multiplying by the plutonium-236 fraction of the total activity as determined by alpha spectrometry.

8.2.2 The activity concentration (AC in dpm plutonium-236/ml) of the stock tracer is calculated from:

$$AC = \frac{(c_{2\pi})(f_6)}{(E_{2\pi})(v)(t)} \qquad (8.2.1)$$

in which $c_{2\pi}$ = the net counts of the evaporated source on the 2π counter,

$E_{2\pi}$ = the counting efficiency of the 2π counter,

v = the volume of stock tracer used to prepare the evaporated source (ml),

t = the duration of the count for the evaporated source on the 2π counter (min)

and f_6 = the ratio of the net counts in the plutonium-236 energy region to the net counts in the entire 3-8 MeV energy region in the alpha spectrum of the electroplated tracer source.

8.2.3 The plutonium-236 activity (T in dpm) added to the sample to trace the plutonium recovery through the analysis is calculated as:

$$T = (AC)(D)(V)(e^{-\lambda t}) \qquad (8.2.2)$$

in which AC = the activity concentration of the stock tracer solution (dpm plutonium-236/ml),

D = the dilution factor in preparing the

working tracer from the stock tracer,

V = the volume of working tracer added to the sample (ml),

and $e^{-\lambda t}$ = the decay correction for plutonium-236 for the time interval between the date of tracer calibration and date of sample analysis.

8.3 CALCULATION OF PLUTONIUM CONCENTRATIONS IN THE ALIQUOT OF SOIL TAKEN FOR ANALYSIS

8.3.1 The concentration of plutonium-239 or plutonium-238 in the aliquot of soil taken for analysis (X_i in dpm/g) is calculated from:

$$X_i = \frac{(C_i)(T)}{(C_6)(W)} \qquad (8.3.1)$$

in which C_i = the net sample counts in the plutonium-239 or plutonium-238 energy region of the alpha spectrometer,

C_6 = the net sample counts in the plutonium-236 energy region of the alpha spectrometer,

T = the activity of plutonium-236 tracer added to the sample (dpm),

and W = the weight of the soil aliquot taken for analysis (g).

8.3.2 The above calculation assumes that the plutonium-236 tracer used in the analysis is sufficiently

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free from plutonium-238 and plutonium-239 activities (<0.1%) to cause negligible interference in the plutonium determinations. Older supplies of plutonium-236 (pre 1974) may contain appreciable amounts of plutonium-238 and/or plutonium-239 (up to 1-2%) and should not be used. If the poorer grade tracer is used, a freshly purified portion must be assayed for plutonium-236, plutonium-238 and plutonium-239 by alpha spectrometry and the necessary corrections for adding plutonium-238 and plutonium-239 to the sample with the tracer must be made.

8.4 CALIBRATION OF THE ALPHA SPECTROMETER AND CALCULATION OF THE PLUTONIUM RECOVERY

8.4.1 The absolute counting efficiency of the alpha spectrometer (E_s) must be determined in order to evaluate the plutonium recovery through the analytical procedure. Americium-241 electroplated in the same manner as the samples should be used for this purpose. The spectrometer counting efficiency may be calculated from:

$$E_s = \frac{(r_s)(E_{2\pi})}{r_{2\pi}} \qquad (8.4.1)$$

in which r_s = the net counting rate of the electroplated source over the entire energy region on the alpha spectrometer (cpm),

$r_{2\pi}$ = the net counting rate of the same source on the 2π counter (cpm),

and $E_{2\pi}$ = the counting efficiency of the 2π counter.

8.4.2 The plutonium recovery through the analysis (Y) is calculated from:

$$Y = \frac{R_6}{(T)(E_s)} \qquad (8.4.2)$$

in which R_6 = the net counting rate in the plutonium-236 energy region of the alpha spectrum of the sample (cpm).

8.5 PROPAGATION OF UNCERTAINTIES

8.5.1 The uncertainties associated with the plutonium-236 tracer calibration and the soil analysis are estimated from the 2σ or 95% confidence level (95% C.L.) uncertainties of all appropriate radioactivity counts, weighings, pipetings, dilutions and measurements of counting times.

8.5.2 The 2σ or 95% C.L. uncertainty in a net radioactivity count, $C = G - B$, is:

$$\pm 2\sqrt{G + B}$$

in which G = the gross number of counts collected

and B = the expected number of background counts during the same time interval.

The uncertainties in the other variables are determined experimentally by replicate calibrations.

8.5.3 For linear addition or subtraction of independent variables, uncertainties are propagated by taking the square root of the sum of the squares of the individual uncertainties.

8.5.4 For linear multiplication and division of independent variables, the fractional uncertainty in the final result is obtained by taking the square root of the sum of the squares of the fractional errors in each of the independent variables.

SAMPLE CALCULATIONS

1. CALIBRATION OF THE 2π ALPHA COUNTER

1.1 The NBS certified americium-241 standard (3.23×10^5 dpm ± 1%) was counted on the 2π alpha counter for 10.00 ± 0.02 minutes. The total number of counts collected was 1,564,612 ± 2500 at the 95% C.L. (2σ).

1.2 The 2π counting efficiency calculated from equation (8.1.1) is:

$$E_{2\pi} = \frac{1{,}564{,}612 \pm 2500^*}{(3.23 \times 10^5)(10.00 \pm 0.02)(1.023)}$$

$$= 0.474 \pm 0.001$$

2. STANDARDIZATION OF THE PLUTONIUM-236 TRACER

2.1 The first evaporated source of 1.029 ± 0.002 ml of the stock plutonium-236 tracer gave 61,124 ± 494 net counts for a 250.0 ± 0.0 minute count on the 2π counter. The electroplated tracer counted for 250 minutes on the alpha spectrometer yielded 51,460 net counts in the plutonium-236 energy region and 62 net counts in the rest of the 3-8 MeV energy region giving a correction factor (f_6) of $[51460/(51460 + 62)] \pm 2[(51460)(62)/(51460 + 62)^3]^{1/2}$ or 0.999 ± 0.000 to be applied to the 2π count. (Sill 1975a)

* To avoid confusion, experimentally observed values were not rounded off in all equations. The calculated results, however, have been rounded off to the appropriate number of significant figures for the given situation.

2.2 The activity concentration (AC) of the plutonium-236 tracer calculated from equation (8.2.1) is:

$$AC = \frac{(61{,}124 \pm 494)(0.999 \pm 0.000)}{(0.474 \pm 0.001)(1.029 \pm 0.002)(250.0 \pm 0.0)}$$

$$= 501 \pm 4 \text{ dpm plutonium-236/ml at the 95\% C.L.}$$

2.3 The second evaporated source yielded an activity concentration value of 495 ± 4 dpm plutonium-236/ml.

2.4 Averaging the two values the activity concentration of the stock tracer is:

AC = 498 ± 3 dpm plutonium-236/ml at the 95% C.L.

3. CALCULATION OF PLUTONIUM-239 AND PLUTONIUM-238 CONCENTRATIONS IN THE ALIQUOT OF SOIL TAKEN FOR ANALYSIS

3.1 A 1.002 ± 0.002 ml aliquot of working plutonium-236 tracer (stock tracer diluted 1.029 ± 0.002 to 49.8 ± 0.01) was added to 10.0 ± 0.1 grams of the -10 mesh fraction of the soil sample and the analysis was performed 65 days after the calibration of the stock tracer ($e^{-\lambda t} = 0.958$). A 1134-minute spectrometer count of the sample yielded the following data:

Energy Region	Gross Counts	Background Counts	Net Counts ± 2σ
Plutonium-236	1953	10	1943 ± 89
Plutonium-239	1394	6	1388 ± 75
Plutonium-238	215	8	207 ± 30

3.2 The amount of plutonium-236 tracer added (T in dpm) is calculated from equation (8.2.2):

$$T = (498 \pm 3)\left(\frac{1.029 \pm 0.002}{49.8 \pm 0.01}\right)(1.002 \pm 0.002)(0.958)$$

$$= 9.88 \pm 0.07 \text{ dpm plutonium-236}$$

3.3 The plutonium-239 and plutonium-238 concentrations in the -10 mesh fraction taken for analysis are calculated from equation (8.3.2):

$$X_9 = \frac{(1388 \pm 75)(9.88 \pm 0.07)}{(1943 \pm 89)(10.0 \pm 0.1)}$$

$$= 0.71 \pm 0.05 \text{ dpm plutonium-239/g}$$

$$X_8 = \frac{(207 \pm 30)(9.88 \pm 0.07)}{(1943 \pm 89)(10.0 \pm 0.1)}$$

$$= 0.11 \pm 0.02 \text{ dpm plutonium-238/g}$$

4. CALIBRATION OF THE ALPHA SPECTROMETER AND CALCULATION OF THE PLUTONIUM RECOVERY

4.1 The electroplated americium-241 source (Section 6.1.4) yielded 206,741 ± 909 net counts in the 3-8 MeV energy range for a 100.0 ± 0.0 minute count on the alpha spectrometer. A 100.0 ± 0.0 minute count of the same source on the 2π counter yielded 465,093 ± 1363 net counts.

4.2 The counting efficiency of the spectrometer (E_s) is calculated from equation (8.4.1):

$$E_s = \frac{(2067 \pm 9)(0.474 \pm 0.001)}{(4651 \pm 14)}$$

$$= 0.211 \pm 0.001$$

5.3 The plutonium recovery for the analysis of the soil sample calculated from equation (8.4.2) is:

$$Y = \frac{(1943 \pm 87)/1134}{(9.88 \pm 0.07)(0.211 \pm 0.001)}$$

$$= 0.82 \pm 0.04$$

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